Control over tuning fullerene microcrystals by means of engineering charge transfer interactions

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ABSTRACT: Multifunctional fullerene microcrystals have been prepared by the instruction of water in the liquid-liquid interfacial precipitation. The resulting microcrystals were characterized microscopically and spectroscopically. The role of water in engineering charge transfer interactions between fullerenes and electron donating solvents have been corroborated through thermogravimetric and transient absorption spectroscopy analysis.

KEYWORDS: fullerene, crystal, morphology, charge transfer

1. INTRODUCTION

Fullerene C_{60} owns unique properties and attracts lots of attention since its discovery.[1] In recent years, its ability to form 1-D rods,[2-4] tubes,[5-7] 2-D plates,[8,9] and 3-D particles[10,11] render it useful for potential applications in biological field,[12] catalyst carriers,[13] electro-chemical or electro-analytical applications,[14] field-effect transistors,[15] fuel cells,[16] photonics and solar cells[17] etc. Meanwhile, several synthetic methodologies have been developed, such as templates method,[18] evaporation method,[11,19] and liquid-liquid interfacial precipitation (LLIP)

method,[3,5,8,9] to control the broad variety of fullerene crystals. LLIP method stands out among them with its broad advantages including high repetition rate, simple preparation process etc. It has transcended into a reliable way to construct 1-D fullerene micro/nanofibers (FM/NFs) with controllable characteristics. Moreover, the ways and means to prepare diverse fullerene micro/nanocrystals in different dimensions making use of, for example, the hydrophobic nature of fullerenes have been explored. In 2009, Sathish et al. demonstrated the controlled formation of 2D C_{60} sheets by simple solvent treatment and by introducing water in the preparation route.[9] In 2010, Miyazawa et al. discussed the effect of water on the growth of C_{60} nanowhiskers in toluene system and concluded that by using isopropanol/water mixture as poor solvent, granular fullerene crystals could be fabricated.[20] Also in 2010, Zhang et al. assembled closely-packed and orderly-oriented C_{60} nanorod bundles by introducing water into LLIP method when using m-xylene.[21]

Benzene, toluene, and m-xylene are similar in nature and all show good fullerene solubility. Quite different are solvents that have a nitrogen atom such as n-methyl-2-pyrrolidone (NMP) or pyridine, which has a lone pair, and could behave as electron donors. In former studies, the existence of charge transfer interactions leads to the formation of different and interesting structures.[22,23] Studies regarding the understanding and taking advantage of charge transfer reactions in constructing different fullerene micro/nanocrystals have never been carried out to this date. In this paper, by simple adding water to the anti-solvent isoproponal (IPA) and suppressing electron donor-acceptor interactions[24,25] between electron accepting fullerenes and electron donating solvents such as NMP, pyridine, and aniline, we realized morphologies ranging from fibers to particles.

2. RESULTS AND DISCUSSION

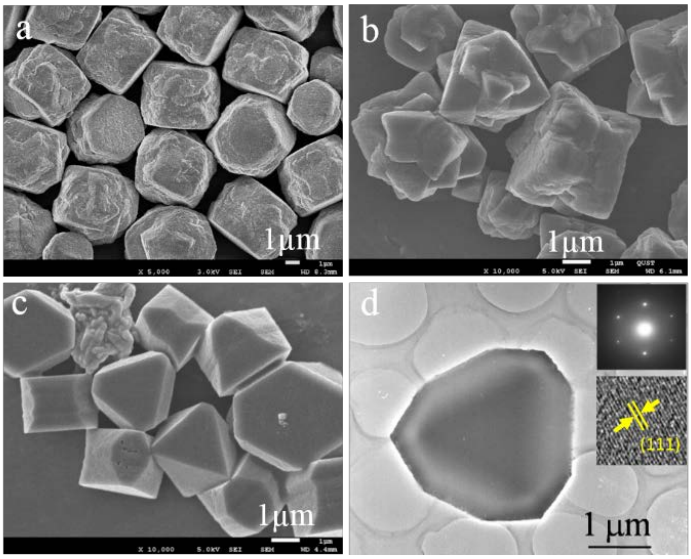

Figure 1. SEM images of FMPs prepared in (a) NMP, (b) pyridine and (c) aniline. (d) shows the TEM images of FMPs prepared in aniline. The insert shows the SEAD pattern and HRTEM image.

As shown in Figure 1, the SEM images corroborate that different fiber morphologies were prepared in the absence of water, (Figure S1) while uniform fullerene microparticles (FMPs) with sizes around 5 μm have been realized when using the anti-solvent in the presence of water. Due to the different nature of the solvents, the morphologies of FMPs varies from hexagonal cylindrical, flower-shaped to polyhedron under the use of different good solvents - NMP, pyridine, and aniline, separately.

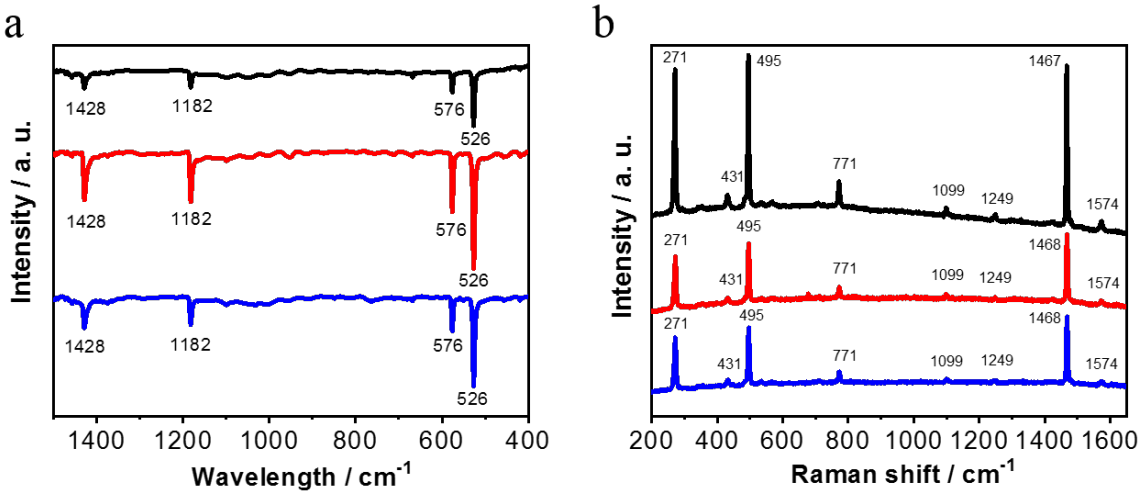

Figure 2. (a) FT-IR and (b) Raman spectra of FMPs prepared in NMP (black), pyridine (red) and aniline (blue).

Although different in morphology, FMPs featured the same crystal structure of face centered cubic (a=1.44 nm) that was seen for FMFs. (Figure S2) Meanwhile, the FT-IR spectra for all samples reveal four major C60 characteristic peaks at 526, 576, 1182 and 1428 cm^{-1}. (Figure 2a) The Raman peaks appearing at 271, 431, 495, 771, 1099, 1249, 1468 and 1574 cm^{-1} are attributed to the Hg and Ag modes of C_{60}. (Figure 2b) Compared with pristine powder of C_{60}, no appreciable shifts have been observed, indicating crystallization rather than polymerization. Thermogravimetric analysis as shown in Figure 3, show, on one hand, for FMPs a single weight loss at around 800 ℃ as a result of the C_{60} sublimation. FMFs, on the other hand, an additional weight loss of 11.1% starting from 200 ℃ due to the loss of the solvents trapped inside the crystals.[26,27] Through the conversion of the weight loss percentages, it is concluded that the molar ratio of NMP to C_{60} in FMFs is approximately 1:1.

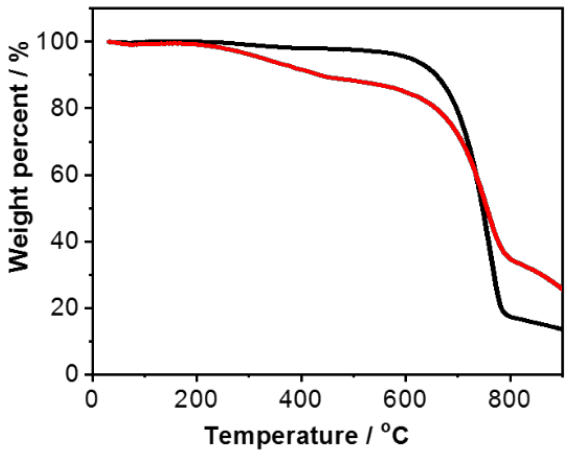

Figure 3. Thermogravimetric analysis of FMPs (black) and FMFs (red) prepared using NMP.

To further explore the differences between FMFs and FMPs, transient absorption measurements have been conducted using 387 nm excitation. For FMPs, within the first few picoseconds, the singlet excited state of C_{60} with its characteristic 550 and 910 nm feature has been populated as shown in Figure 4a. Once formed, the C_{60} singlet excited state undergoes intersystem crossing to afford the corresponding triplet excited state of C_{60} with its characteristic at around 750 nm.[28] The lifetimes of the C_{60} singlet and triplet excited states in the FMPs are 6.0 ps and 12.9 ns. For the FMFs, a different excited state deactivation is noted. A closer look at the decay of the singlet excited state of C_{60} reveals the parallel population of the triplet excited state of C_{60} around 750 nm

and the one-electron reduced form of C_{60} around 1020 nm.[29] From the latter we conclude a charge separation involving C_{60} and the electron donating solvent. A fast charge recombination with a lifetime of 11.9 ps follows the charge separation. The absorption features of the charge separated state are weak in the FMFs, but completely absent in the case of FMPs.

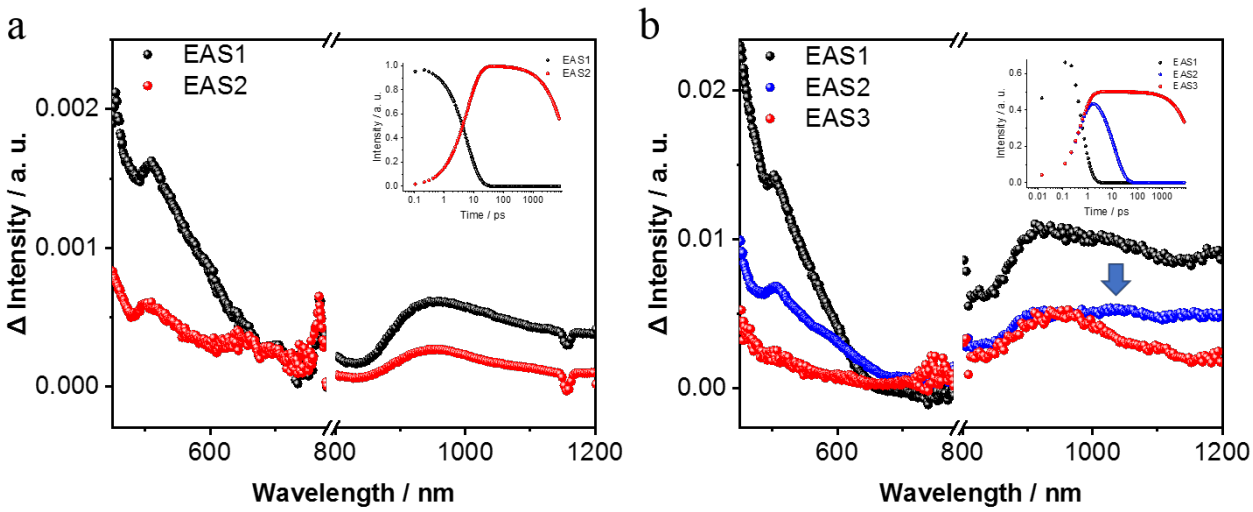

Figure 4. (a) Evolution associated spectra of the C_{60} singlet excited state (EAS1, black) and the C_{60} triplet excited state (EAS3, red) in FMPs. The insert shows the population-time profiles obtained from Global and Target analysis of the sequential decay from the C_{60} singlet excited state (EAS1, black) to the C_{60} triplet excited (EAS3, red). (b) Evolution associated spectra of the C_{60} singlet excited state (EAS1, black), the charge separated state (EAS2, blue) and the C_{60} triplet excited state (EAS3, red) in FMFs. The insert shows the population-time profiles obtained from Global and Target analysis of the parallel decay from the C_{60} singlet excited state (EAS1, black) to the charge separated state (EAS2, blue) and the C_{60} triplet excited state (EAS3, red). For differential absorption spectra changes of FMPs and FMFs, please see Figure S4.

Considering the TGA results, it is reasonable to postulate that the difference in terms of charge transfer lies in the preparation conditions, which either lead to FMFs or FMPs. When forming FMFs, the C_{60} singlet excited state deactivation is dominated by a charge transfer. In the preparation of FMPs, the participation of water breaks the electron donor-acceptor interactions between C_{60} and the respective solvents as well as the anisotropic nucleation, which leads, in turn, to the formation of particles and not fibers.

3. CONCLUSION

In conclusion, with the objective to design multifunctional fullerene microcrystals we have employed the LLIP method based on IPA as anti-solvent in the absence or presence of water. Not only that water is decisive in the overall morphology, that is, FMPs versus FMFs, but also its assist in modulating charge transfer interactions both in the ground and excited state. In the context of the latter, full control over activation/deactivation of charge transfer interactions in the design of multifunctional fullerene microcrystals brings the fundamental consequence of charge separation upon photoexcitation. As such, our work has the potential to (re)shape the fields, where fullerene crystallization is essential: optoelectronic devices, in general, and solar cells, photodetectors, light emitting devices, in particular.

4. Experimental Section

In preparation process, LLIP method was used.[23] In the preparation of FMPs, C_{60} powder was mixed with NMP, pyridine or aniline to get saturated C_{60} solution through ultrasonication and filtration. Then, 1 ml C_{60} saturated solution was mixed with 9 ml aqueous isopropyl alcohol which contains 1 ml distilled water. The mixtures were ultrasonicated for 10 min (40 KHz, 50 w, 8℃) and afterwards incubated for 24 h at 8℃ to get uniform FMPs. In the preparation of FMFs, all the procedures work the same, but no water have been added. A diagram to show the preparation process is shown in Scheme S1. For the information of the characterization methods, please see supporting information and references 23 and 30.

ASSOCIATED CONTENT

Supporting Information. Characterization methods, Preparation schematic diagram, Additional SEM image, Raman spectra, XRD patterns and Different absorption spectra. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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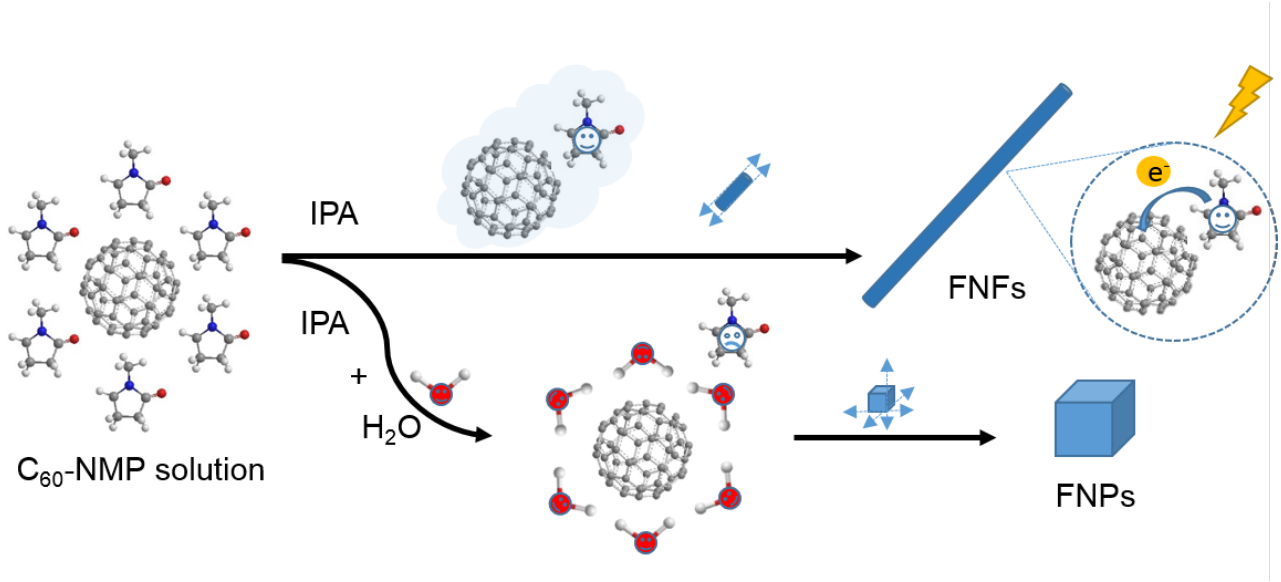
IPA
IPA
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C_{60}-NMP solution
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Supporting information

Control over tuning fullerene microcrystals by means of engineering charge transfer interactions

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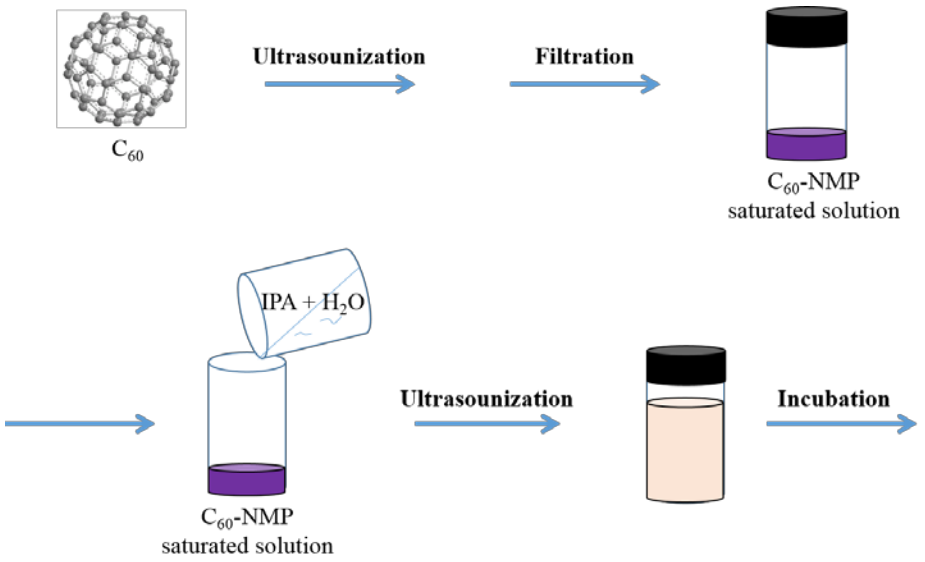

Scheme S1 The preparation route of FMPs.

The morphologies of FMPs were characterized using scanning electron microscope (SEM, JEOL JSM-6700F) transmission electron microscopy (TEM, JEOL JEM-2000EX). The composition and crystal structure of FMPs were characterized using Raman micro-spectroscope (Renishaw 2000 spectrometer, 785 nm laser), Fourier transformation infrared (FT-IR, Bruker Vertex 70), X-ray diffraction (XRD, Rigaku D-Max 2500/PC, Ni-filtered Cu-Kα radiation (λ=1.5418 Å)) and thermo gravimeter (TG, Mettler Toledo DSC1-700).[1] During the TG experiment, 2 mg of the samples were selected in nitrogen atmosphere from room temperature to 900℃ at the heating rate of 5℃/min. Femtosecond transient absorption spectra were obtained with a Ti:sapphire laser system CPA-2101 (Clark-MXR, Inc.) in combination with a Helios TAPPS detection unit from Ultrafast Inc. The initial laser excitation wavelength is 775 nm with a pulse width of 150 fs. The used excitation wavelength was 387 nm, which was generated with a SHG crystal. For the generation of the white light a sapphire crystal of adequate thickness was used. The chirp-effect between 420 and 770 nm is approximately 350 fs. The detection was carried out with two CCD cameras, each for a specific measuring range. The spectral window is therefore 415 to 770 nm and 770 to 1600 nm. The delay line allows spectral acquisition up to time delays of 8000 ps.[2] All samples were measured in concentrated suspensions in the same solvents we used to prepare the samples in fused quartz glass cuvettes with a thickness of 2 mm.[3,4] Data was acquired with the software HELIOS Visible/nIR (Newport / Ultrafast Systems).

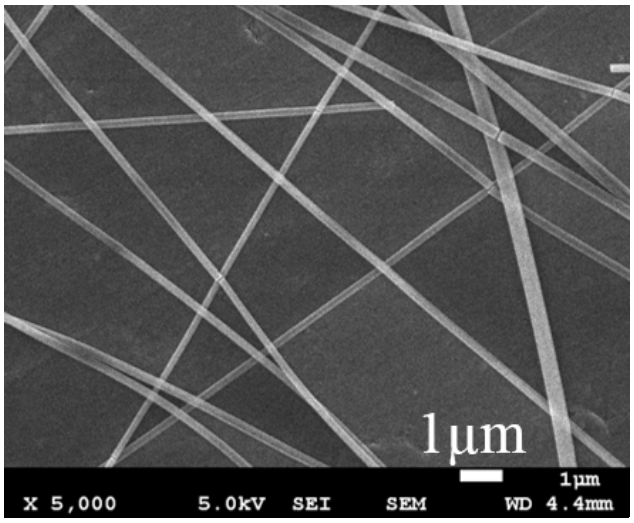

Figure S1. SEM image of FMFs prepared in NMP.

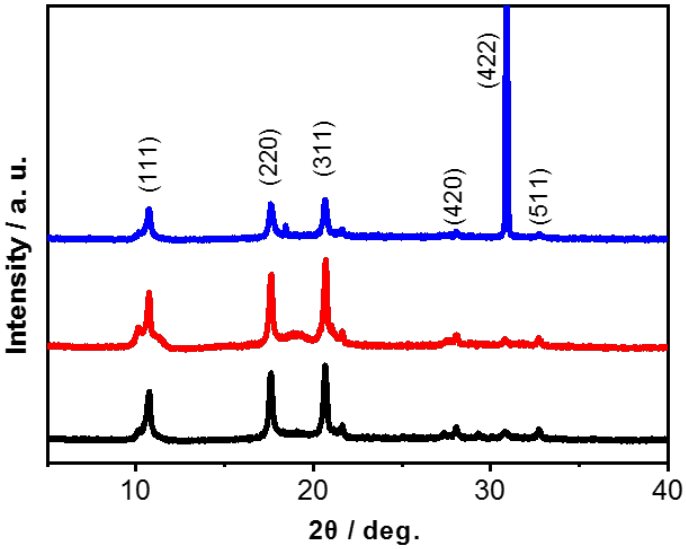

Figure S2. XRD patterns of FMPs prepared in NMP (black), pyridine (red) and aniline (blue).

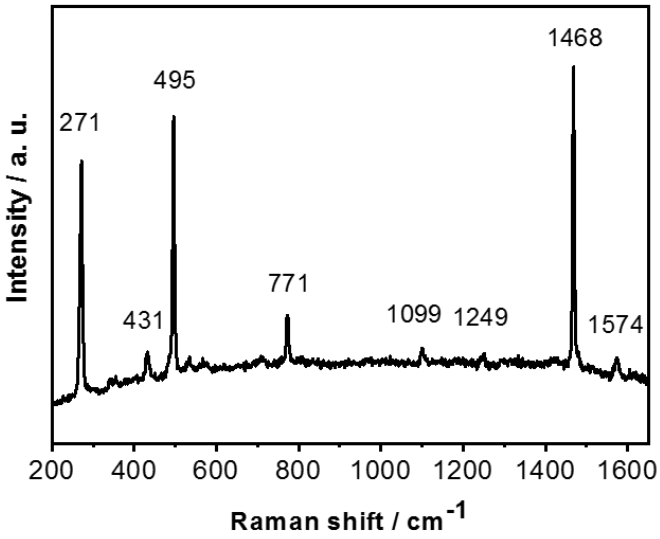

Figure S3. Raman spectrum of FMFs prepared in NMP.

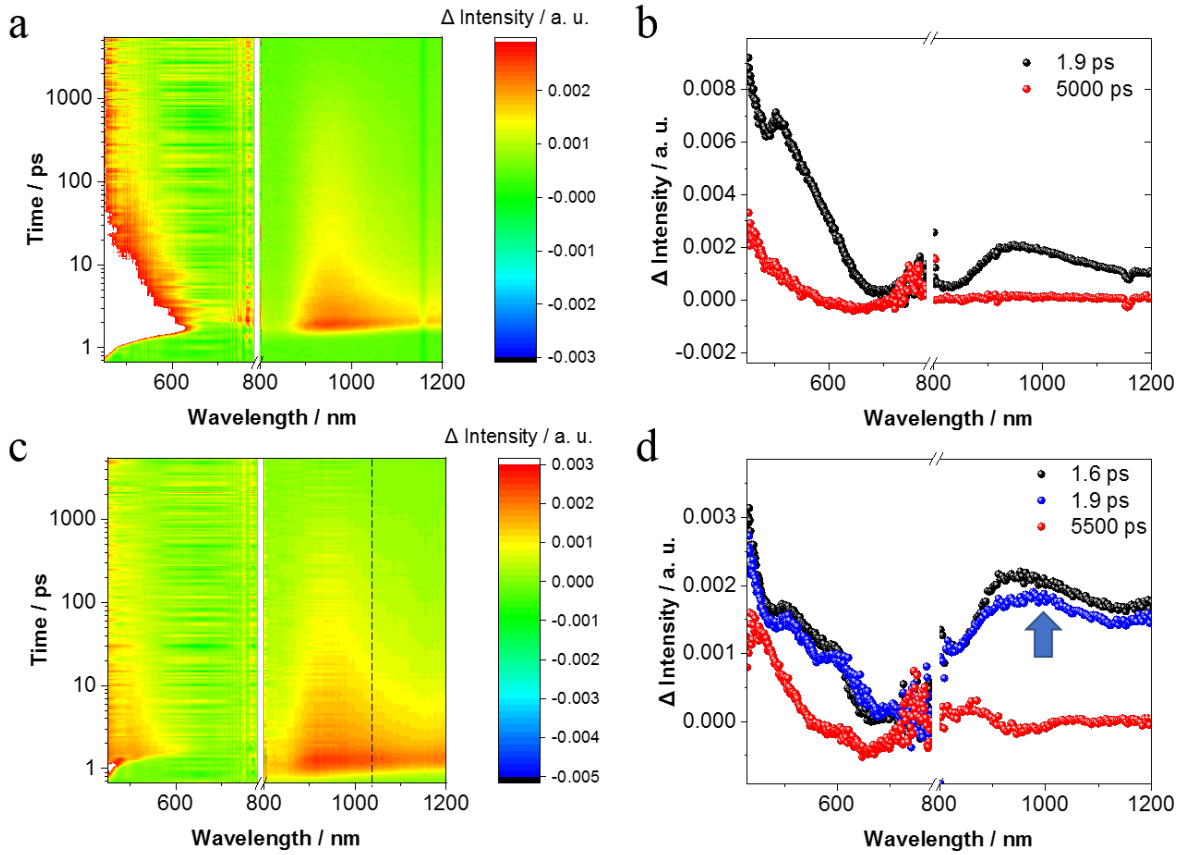

Figure S4. (a) Differential absorption spectra changes obtained upon femtosecond pump-probe experiments (387 nm / 500 nJ) of FMPs prepared in NMP. (b) Differential absorption spectra obtained upon femtosecond pump-probe experiments of FNPs prepared in NMP with time delays of 1.9 and 5000 ps. (c) Differential absorption spectra changes obtained upon femtosecond pump-probe experiments (387 nm / 500 nJ) of FMFs prepared in NMP. (d) Differential absorption spectra obtained upon femtosecond pump-probe experiments of FNPs prepared in NMP with time delays of 1.6, 1.9 and 5500 ps.

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